

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

25 August 2000 (25.08.00)

International application No.

PCT/GB00/00060

Applicant's or agent's file reference

SMC 60340/WO

International filing date (day/month/year)

12 January 2000 (12.01.00)

Priority date (day/month/year)

04 February 1999 (04.02.99)

Applicant

ROTHWELL, Geoffrey, Richard et al

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
13 July 2000 (13.07.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SMC 60340/W0	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/GB 00/ 00060	International filing date (day/month/year) 12/01/2000	(Earliest) Priority Date (day/month/year) 04/02/1999
Applicant AVECIA LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00060

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 837 046 A (TATUM JOHN PHILIP ET AL) 17 November 1998 (1998-11-17) column 3, line 51-62; claims 1,2,4; example 1	1,3-11, 14-17
Y	---	12,13
Y	WO 97 15633 A (TATUM JOHN P ;WOODS JILL (GB); XAAR LTD (GB)) 1 May 1997 (1997-05-01) cited in the application page 8, line 1 -page 9, line 7	12,13
X	GB 2 001 083 A (ICI LTD) 24 January 1979 (1979-01-24) cited in the application page 2, line 51,52; example 23 --- -/-	1-8,10, 14,16

☒

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 March 2000

Date of mailing of the international search report

03/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rousseau, F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00060

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No:
X	<p> DATABASE WPI Derwent Publications Ltd., London, GB; AN 1987-046767'25! XP002132649 & JP 62 004433 A (DAINIPPON INK & CHEM KK ; KAWAMURA INST CHEM RES), 10 January 1987 (1987-01-10) abstract ----- </p>	<p> 1-5, 8, 10, 14, 16 </p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00060

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5837046	A	17-11-1998	CA 2212551 A EP 0808347 A WO 9624642 A JP 2990378 B JP 10507487 T	15-08-1996 26-11-1997 15-08-1996 13-12-1999 21-07-1998
WO 9715633	A	01-05-1997	BR 9611332 A CA 2233482 A EP 0857196 A JP 11501353 T	14-09-1999 01-05-1997 12-08-1998 02-02-1999
GB 2001083	A	24-01-1979	AU 518818 B AU 3780278 A BE 868890 A CA 1117689 A CH 640150 A DE 2830860 A DK 317278 A, B, FR 2397226 A IT 1097525 B JP 1570685 C JP 54037082 A JP 63030057 B NL 7807584 A, C NZ 187714 A US 4224212 A	22-10-1981 10-01-1980 10-01-1979 02-02-1982 30-12-1983 01-02-1979 16-01-1979 09-02-1979 31-08-1985 25-07-1990 19-03-1979 16-06-1988 17-01-1979 12-09-1980 23-09-1980
JP 62004433	A	10-01-1987	NONE	

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receipt Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) SMC 60340/WO

Box No. I TITLE OF INVENTION

Printing Inks

B x No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Avecia Limited
Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

☐ This person is also inventor.

Telephone No.

0161 740 1460

Facsimile No.

0161 721 5801

Teleprinter No.

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant
for the purposes of:

☐ all designated
States

☒ all designated States except
the United States of America

☐ the United States
of America only

☐ the States indicated in
the Supplemental Box

B x No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ROTHWELL, Geoffrey Richard
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box
is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant
for the purposes of:

☐ all designated
States

☐ all designated States except
the United States of America

☒ the United States
of America only

☐ the States indicated in
the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf
of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

FAWKES, David Melville
Intellectual Property Group
Avecia Limited
PO Box 42, Hexagon House
Blackley, Manchester M9 8ZS
United Kingdom

Telephone No.

0161 721 2038

Facsimile No.

0161 721 5801

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box N . III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

THETFORD, Dean
PO Box 42, Hexagon House
Blackløy
Manchester M9 8ZS
United Kingdom

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; **at least one must be marked**):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IS Iceland | |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> ZA South Africa |
| | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KR Republic of Korea | |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |
| <input checked="" type="checkbox"/> LC Saint Lucia | |
| <input checked="" type="checkbox"/> LK Sri Lanka | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- | | |
|---|--|
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> DM Dominica |
| <input checked="" type="checkbox"/> MA Morocco | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

Supplemental Box If the Supplemental Box is not used, this sheet should not be included in the request.

1. If, in any of the Boxes, **the space is insufficient** to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) **if more than two persons are involved as applicants and/or inventors** and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) **if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked:** in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) **if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America:** in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) **if, in addition to the agent(s) indicated in Box No. IV, there are further agents:** in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) **if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part":** in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) **if, in Box No. VI, there are more than three earlier applications whose priority is claimed:** in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) **if, in Box No. VI, the earlier application is an ARIPO application:** in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the **precautionary designation statement** contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning **non-prejudicial disclosures or exceptions to lack of novelty:** in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Continuation of Box IV

MAYALL, John
NELSON, Michael Andrew
PUGSLEY, Roger Graham
REVELL, Christopher
SCHMITT, Maja
SHELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom

LOCKE, Timothy John

of Intellectual Property Group, Avecia Limited, PO Box 2, Belasis Avenue, Billingham, Cleveland TS23 1YN, United Kingdom

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 4 February 1999 04/02/1999	9902386.3	GB		
item (2)				
item (3)				

☐ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s):

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen: the two-letter code may be used):

ISA / EPO

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 05
description (excluding sequence listing part) : 11
claims : 02
abstract : 01
drawings : -
sequence listing part of description : 00

Total number of sheets : 19

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☒ priority document(s) identified in Box No. VI as item(s): **1**
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ other (specify):

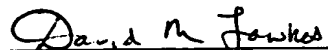
Figure of the drawings which should accompany the abstract:

Language of filing of the international application: **ENGLISH**

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

For Avecia Limited - G.R.Rothwell and D.Thetford



FAWKES, David Melville

For receiving Office use only		2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60340/WO	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB00/00060	International filing date (<i>day/month/year</i>) 12/01/2000	Priority date (<i>day/month/year</i>) 04/02/1999	
International Patent Classification (IPC) or national classification and IPC C09D11/00			
Applicant AVECIA LIMITED et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 13/07/2000	Date of completion of this report 29.05.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Rousseau, F Telephone No. +49 89 2399 8297



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/00060

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
Description, pages:

1-11 as originally filed

Claims, No.:

1-16 as received on 23/11/2000 with letter of 22/11/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/00060

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	11,12,14-16
	No:	Claims	1-10,13
Inventive step (IS)	Yes:	Claims	
	No:	Claims	11,12,14-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations **see separate sheet**

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/00060

1. Amended claims 1 to 16 meet the requirements of Art. 34(2)b) PCT. It is pointed out that the definition of present claim 1 does not exclude that the dispersant might be present as a salt thereof, because in that case Z is also the residue of a polyamine or polyimine.
2. US-A-5 837 046 (D1) discloses in claims 1, 2 and 4 and in example 1 a drop on demand ink jet printing ink comprising a pigment, a mixture of an aliphatic hydrocarbon and oleyl alcohol as a non-aqueous medium, a fluidising agent and a dispersant, which is the reaction product of a poly(lower alkylene-imine) with a polyester having a free carboxylic acid group in which there at least two polyesters chains attached to each poly(lower alkylene-imine) chain. According to column 3, lines 51-62 of the same document, the dispersants to be used are especially those described in GB-A-2 001 083 (D2). The dispersant "Agent E" described in page 4 of D2 falls under the definition of the dispersant given in present claims 1 and 3-6. Since D1 especially teaches the skilled reader to use the dispersants disclosed in D2, to which belong "Agent E", D1 is considered to disclosed an ink jet printing ink comprising a pigment, a non-aqueous medium as defined in D1 and "Agent E" as a dispersing agent. Hence, the subject-matter of present claims 1, 3-10 and 13 is deemed to lack novelty in view of D1 (Art. 33(2) PCT).

The ink disclosed in example 23 of D2, which contains a pigment, toluene and agent E, appears to be suitable for ink jet printing. Moreover, D2 discloses in page 2, lines 51-52, that the weight ratio of polyester to polyalkylene imine in the dispersion agent can range from 1 to 10. Therefore, the subject-matter of present claims 1-7, 9 and 13 is anticipated by D2 (Art. 33(2) PCT).

According to its abstract in Derwent (AN:1987-046767 [25]), JP-A-62004433 (D3) discloses inks comprising a pigment, toluene, a dispersant, which is the reaction product of polyoctamethylene polyamine of formula $H_2N-((CH_2)_8NH)_{1-5}-(CH_2)_8NH_2$ with a polyester having 20-120 acid value and formed by dehydration of 12-hydroxystearic acid (i.e. comprising between 1.6 and 9.85 repeating units). The abstract discloses a weight ratio of polyester to polyamine of 10.2. The subject-matter of present claims differs from D3 in that the M_n of Z is from 5 000 to 100 000.

3. As far as the use of dispersants which are not in the salt form is concerned, the subject-matter of present claims 1 and 3 to 16 lacks an inventive step over D1 (Art. 33(3) PCT). Closest prior art is an ink jet printing ink formulation according to D1 which comprises the dispersant "Agent E" as defined in D2, since D1 especially teaches the skilled reader to use the dispersants disclosed in D2, to which belong "Agent E". In the absence of any evidence that the use of the dispersant which is not in its salt form solves a technical problem in a manner that the skilled person would consider as unexpected, one has to conclude that the subject-matter of claims 1 and 3 to 10 lacks an inventive step within the meaning of Art. 33(3) PCT, since the teaching of D2 is not limited to the use of the dispersants in their salt form (see claim 2 of D2). It is pointed out that the additional features contained in claims 11 and 12 are conventional in the field of ink jet printing inks as shown by WO97/15633 (D4) (see passage from page 8, line 1 to page 9, line 7). Thus, if a skilled person starting from D1 wanted merely to provide further drop on demand ink jet printing inks, it would have been obvious for him in view of D4 to add a linear phenolic polymer as RMV modifier. Printing an image on a substrate by means of a drop on demand ink jet printing ink or a cartridge comprising a drop on demand ink jet printing ink are conventional features in the art and have not been shown to contribute to inventive step either.

In view of examples 1 to 3 and comparative example A (see pages 7 and 8 of the present application), the objective technical problem solved by the use of a weight ratio of $(T-(O-A-CO)_n -)_p$ to Z from 9:1 to 13:1 can be seen as to provide inks having a higher Receding Meniscus Velocity. None of the documents cited in the international search report suggests that this result could be obtained by selecting a weight ratio of $(T-(O-A-CO)_n -)_p$ to Z from 9:1 to 13:1. Hence, as far as the use of dispersants which are not in the salt form is concerned, the subject-matter of present claim 2 appears to meet the requirements of Art. 33(3) PCT.

4. The subject-matter of present claims is industrially applicable (Art. 33(4) PCT).

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference SMC 60340/WO		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/00060	International filing date (day/month/year) 12/01/2000	Priority date (day/month/year) 04/02/1999	
International Patent Classification (IPC) or national classification and IPC C09D11/00			
Applicant AVECIA LIMITED et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 2 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 			
Date of submission of the demand 13/07/2000		Date of completion of this report 29.05.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Rousseau, F Telephone No. +49 89 2399 8297	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/00060

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/00060

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1. Statement

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	No:	Claims	1-10,13
Inventive step (IS)	Yes:	Claims	
	No:	Claims	11,12,14-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations **see separate sheet**

1. Amended claims 1 to 16 meet the requirements of Art. 34(2)b) PCT. It is pointed out that the definition of present claim 1 does not exclude that the dispersant might be present as a salt thereof, because in that case Z is also the residue of a polyamine or polyimine.
2. US-A-5 837 046 (D1) discloses in claims 1, 2 and 4 and in example 1 a drop on demand ink jet printing ink comprising a pigment, a mixture of an aliphatic hydrocarbon and oleyl alcohol as a non-aqueous medium, a fluidising agent and a dispersant, which is the reaction product of a poly(lower alkylene-imine) with a polyester having a free carboxylic acid group in which there are at least two polyester chains attached to each poly(lower alkylene-imine) chain. According to column 3, lines 51-62 of the same document, the dispersants to be used are especially those described in GB-A-2 001 083 (D2). The dispersant "Agent E" described in page 4 of D2 falls under the definition of the dispersant given in present claims 1 and 3-6. Since D1 especially teaches the skilled reader to use the dispersants disclosed in D2, to which belong "Agent E", D1 is considered to disclose an ink jet printing ink comprising a pigment, a non-aqueous medium as defined in D1 and "Agent E" as a dispersing agent. Hence, the subject-matter of present claims 1, 3-10 and 13 is deemed to lack novelty in view of D1 (Art. 33(2) PCT).

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3. As far as the use of dispersants which are not in the salt form is concerned, the subject-matter of present claims 1 and 3 to 16 lacks an inventive step over D1 (Art. 33(3) PCT). Closest prior art is an ink jet printing ink formulation according to D1 which comprises the dispersant "Agent E" as defined in D2, since D1 especially teaches the skilled reader to use the dispersants disclosed in D2, to which belong "Agent E". In the absence of any evidence that the use of the dispersant which is not in its salt form solves a technical problem in a manner that the skilled person would consider as unexpected, one has to conclude that the subject-matter of claims 1 and 3 to 10 lacks an inventive step within the meaning of Art. 33(3) PCT, since the teaching of D2 is not limited to the use of the dispersants in their salt form (see claim 2 of D2). It is pointed out that the additional features contained in claims 11 and 12 are conventional in the field of ink jet printing inks as shown by WO97/15633 (D4) (see passage from page 8, line 1 to page 9, line 7). Thus, if a skilled person starting from D1 wanted merely to provide further drop on demand ink jet printing inks, it would have been obvious for him in view of D4 to add a linear phenolic polymer as RMV modifier. Printing an image on a substrate by means of a drop on demand ink jet printing ink or a cartridge comprising a drop on demand ink jet printing ink are conventional features in the art and have not been shown to contribute to inventive step either.

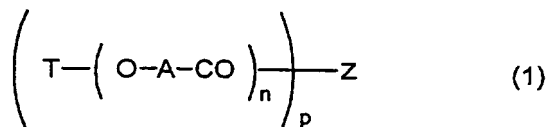
In view of examples 1 to 3 and comparative example A (see pages 7 and 8 of the present application), the objective technical problem solved by the use of a weight ratio of $(T-(O-A-CO)_n-)_p$ to Z from 9:1 to 13:1 can be seen as to provide inks having a higher Receding Meniscus Velocity. None of the documents cited in the international search report suggests that this result could be obtained by selecting a weight ratio of $(T-(O-A-CO)_n-)_p$ to Z from 9:1 to 13:1. Hence, as far as the use of dispersants which are not in the salt form is concerned, the subject-matter of present claim 2 appears to meet the requirements of Art. 33(3) PCT.

4. The subject-matter of present claims is industrially applicable (Art. 33(4) PCT).

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CLAIMS

1. A drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of formula 1



wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene;

Z is the residue of a polyamine or polyimine wherein the number-average molecular weight is from 5,000 to 100,000;

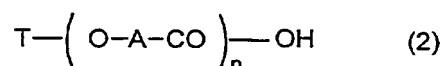
n is from 2 to 10;

p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1.

2. A printing ink as claimed in claim 1 wherein the weight ratio of (T-(O-A-CO)_n)_p to Z is from 9:1 to 13:1.

3. A printing ink as claimed in either claim 1 or claim 2 wherein the dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (TPOAC acid) of formula 2:



wherein T, A and n are as defined in claim 1.

4. A printing ink as claimed in claim 3 wherein the TPOAC acid is derived from 12-hydroxystearic acid.

5. A printing ink as claimed in either claim 3 or claim 4 wherein the number-average molecular weight of the TPOAC acid is from 800 to 2000.

6. A printing ink as claimed in any one of the preceding claims wherein Z is the residue of polyethyleneimine.

SMC 60340

7. A printing ink as claimed in any one of claims 1 to 6 wherein the non-aqueous medium is an aromatic or aliphatic hydrocarbon or mixtures thereof.
8. A printing ink as claimed in claim 7 which additionally comprises a C₁₀₋₃₀-aliphatic fatty alcohol.
9. A printing ink as claimed in any one of claims 1 to 8 wherein the non-aqueous medium has a solubility parameter of 7.0 MPa^{1/2} or less.
10. A printing ink as claimed in any one of claims 1 to 9 which additionally comprises a fluidising agent.
11. A printing ink as claimed in any one of claims 1 to 10 which additionally comprises a Receding Meniscus Velocity (RMV) modifier.
12. A printing ink as claimed in claim 11 where the RMV modifier is a linear phenolic polymer.
13. A printing ink according to any one of the preceding claims wherein the ink has a viscosity at 25°C of less than 50cP.
14. A process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to any one of the preceding claims.
15. A substrate printed with an ink according to any one of claims 1 to 13, or by means of the process according to claim 14.
16. An ink jet printer cartridge containing an ink according to any one of claims 1 to 13.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09D 11/00	A1	(11) International Publication Number: WO 00/46313 (43) International Publication Date: 10 August 2000 (10.08.00)
(21) International Application Number: PCT/GB00/00060 (22) International Filing Date: 12 January 2000 (12.01.00) (30) Priority Data: 9902386.3 4 February 1999 (04.02.99) GB (71) Applicant (for all designated States except US): AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ROTHWELL, Geoffrey, Richard [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). THETFORD, Dean [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). (74) Agents: FAWKES, David, Melville; Intellectual Property Group, Avecia Limited, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB) et al.		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PRINTING INKS (57) Abstract Non-aqueous printing ink for "drop-on-demand" ink jet printers comprising pigment and dispersant which is a polyester chain attached to a polyamine or polyimine chain via amide and/or salt linkages and where the ratio of polyester chain to polyamine or polyimine is from 5:1 to 20:1 by weight. Preferably the polyimine is polyethyleneimine.		

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PRINTING INKS

The present invention relates to non-aqueous printing inks containing pigments and their use in "drop-on-demand" ink jet printers.

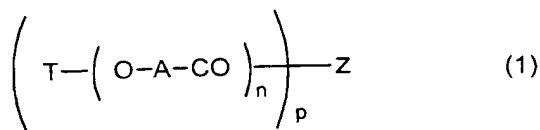
One of the most important class of ink jet printers is the so-called "drop-on-demand" (hereinafter DOD) printer, where droplets of ink are expelled from a print head to make a print mark only when desired to form an image during the printing process. DOD printers use either an electrostatically accelerated ink jet or sequence of droplets which are ejected by pressure impulse actuation. In the latter type of DOD printer, each ink droplet is individually ejected from a nozzle in the print head by means of pressure pulses which are induced, for example, by a piezo-electric actuator acting on the ink in a channel supplying the nozzle or by generation of a vapour bubble in response to a thermal pulse.

One particular problem encountered in continuous printing with ink jet printers is that a small amount of the tail of the droplet being ejected tends to separate from the droplet and collect on that part of the surface of the print head immediately surrounding the nozzle. With high speed printers, there is less opportunity for this tail of the droplet to recede back into the nozzle before the next pressure pulse which results in the build up of an ink residue on the surface of the print head giving a distorted printed mark. This is particularly marked in high dot density printers and especially colour printers. This has led to the introduction of coatings for the print head to reduce the accumulation of such residues but even so the print head still requires cleaning resulting in down-time of the printer.

Improved print performance in DOD printers has been sought by advances in printing ink formulations. Thus, WO 97/15633 discloses a printing ink containing a pigment which is dispersed in a non-aqueous medium using a polyester amine dispersant where some of the basic amine groups in the dispersant are neutralised with an acid or acidic phenolic compound. These printing inks are stated to exhibit a reduction in the amount of residual ink which forms on the print head at the end of each pulse by improving the rate at which the tail of the droplet retreats into the nozzle of the print head. One method of determining the propensity of an ink droplet to retreat back into the nozzle is to measure the Receding Meniscus Velocity (hereinafter RMV) of the printing ink on a surface, such as a fluorosilane coated metal surface. One such method of measuring RMV is described in WO 97/15633.

It has now been found that printing inks exhibiting a superior RMV can be made by dispersing a pigment in a non-aqueous medium by means of a dispersant containing a higher proportion of polyester to those described in WO 97/15633.

According to a first aspect of the present invention there is provided a drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of Formula (1)



5 wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene or alkenylene;

Z is the residue of a polyamine or polyimine;

n is from 2 to 10;

10 p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1; including salts thereof.

The dispersant of Formula 1 is hereinafter referred to as The Dispersant.

When T is a polymerisation terminating group, it is preferably the residue of a carboxylic acid of formula T-COOH wherein T is aliphatic which may be linear or
15 branched, saturated or unsaturated but is preferably linear and preferably saturated. The number of carbon atoms in T can be as high as 50. It is preferred that T contains not less than 8, more preferably not less than 12 and especially not less than 14 carbon atoms. It is also preferred that T contains not greater than 30, preferably not greater than 25 and especially not greater than 20 carbon atoms.

20 Preferably, A contains not less than 10, more preferably not less than 12 and especially not less than 14 carbon atoms.

The integer n is preferably not less than 3 and especially not less than 4. It is also preferred that n is not greater than 8 and especially not greater than 6.

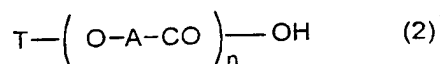
25 The integer p is preferably not greater than 2000 and especially not greater than 1000.

Z is preferably the residue of polyallylamine, polyvinylamine, more preferably poly(C₂₋₄-alkyleneimine) (hereinafter PAI) and particularly poly(ethyleneimine) (PEI).

The PAI may be linear or more preferably branched.

30 The polyamine or polyimine preferably has a number-average molecular weight from 500 to 600,000, more preferably from 1,000 to 200,000, even more preferably from 1,000 to 100,000 and especially from 5,000 to 100,000.

The Dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (hereinafter TPOAC acid) of formula 2:



wherein T, A, and n are as defined hereinbefore.

The number-average molecular weight (M_n) of the TPOAC acid is preferably not less than 500 and especially not less than 800. It is also preferred that the number-average molecular weight of the TPOAC acid is not greater than 3000 and especially not greater than 2000.

The weight ratio of $(T-(O-A-CO)_n)_p$ to Z is preferably not less than 7:1, more preferably not less than 8:1 and especially not less than 9:1. It is also preferred that the weight ratio of $(T-(O-A-CO)_n)_p$ to Z is not greater than 17:1, more preferably not greater than 15:1 and especially not greater than 13:1. Particularly useful effects have been obtained when the weight ratio of $(T-(O-A-CO)_n)_p$ to Z is from 10:1 to 15:1 and especially from 10:1 to 13:1.

The salts of The Dispersants may be those of any inorganic or organic acid including quaternary ammonium salts, particularly those obtainable by reacting The Dispersant with a dialkylsulphate such as dimethylsulphate or an alkylhalide such as ethylchloride.

Preferably, the salt of The Dispersant is that obtained with an organic or inorganic acid. Examples of suitable acids are hydrochloric, sulphuric and acetic acids. The salt may also be that of an acidic phenol or phenolic polymer. Preferably, The Dispersant is in the form of its free-base.

Particularly useful effects have been obtained when the TPOAC acid is derived from ricinoleic acid and especially 12-hydroxystearic acid, particularly commercially available material which contains a small amount of stearic acid as impurity which acts as a polymerisation terminating or end-cap group in the preparation of the TPOAC acid.

The Dispersants are made by a similar process to Example 7/Agent H disclosed in GB 2,001,083.

The pigment may be from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter heading "Pigments". Examples of inorganic pigments are titanium dioxide, zinc oxide, Prussian blue, cadmium sulphide, iron oxides, vermilion, ultramarine and the chrome pigments, including chromates, molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, disazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphendioxazine, quinacridone, perylene, diketopyrrolopyrrole and phthalocyanine series,

especially copper phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although strictly inorganic, behaves more like an organic pigment in its dispersing properties. Preferred organic pigments are phthalocyanines, especially copper phthalocyanines, monoazos, disazos, indanthrones, anthranthrones, quinacridones and carbon blacks.

The printing ink is preferably made by milling the pigment in the non-aqueous medium in the presence of The Dispersant to give a pigment dispersion which is subsequently let down to give the printing ink.

Whereas the non-aqueous may contain up to 2% by weight water it is preferably free from water.

The non-aqueous medium is preferably a substantially non-polar organic liquid.

Substantially non-polar, organic liquids which may be used, either alone or in admixture are aromatic hydrocarbons, such as toluene and xylene, halogenated aliphatic and aromatic hydrocarbons, such as trichloro-ethylene, perchloroethylene and chlorobenzene and particularly aliphatic and aromatic hydrocarbons having at least 6 carbon atoms including mixtures thereof, for example, refinery distillation products and by products.

Preferably, the non-aqueous medium has a polar solubility parameter of not greater than $7.0 \text{ MPa}^{1/2}$ as measured using the method of Hansen, C.M. and Skaarup, K., Journal of Paint Technology, 39 No. 51, 1967, pages 511-514 as described by Patton, T.C. in "Paint Flow and Pigment Dispersion", second edition, Wiley Printerscience, 1979. Examples of non-aqueous media with polar solubility parameters of $7.0 \text{ MPa}^{1/2}$ or less are non-polar organic liquids including mixtures with polar organic liquids wherein the amount of polar liquid is preferably less than 45%, more preferably less than 30%, even more preferably less than 20% and especially less than 10% by weight based upon the weight of the mixture of non-polar and polar organic liquids.

It is especially preferred that the non-aqueous medium with a polar solubility parameter not greater than $7.0 \text{ MPa}^{1/2}$ is an aliphatic hydrocarbon such as those commercially available as Exxsol, Solvesso, Exxon naphtha, Isopar, Pegasol, Lytol and Shellsol.

Particularly suitable non-aqueous media are mixtures of an aliphatic hydrocarbon and a C_{10-30} -aliphatic fatty alcohol which may be linear or branched, saturated or unsaturated. Examples of suitable alcohols are stearyl, lauryl and especially oleyl alcohol.

The dispersion of the pigment in the substantially non-aqueous medium may contain other ingredients which are commonly used in the printing ink industry such as binders, fluidising agents such as those described in GB-A-1508576 and GB-A-2108143, antisedimentation agents, levelling agents and preservatives.

Preferably the ink contains from 2 to 20%, more preferably from 4 to 15% pigment based upon the weight of the ink.

As noted hereinbefore, it is preferable to prepare a concentrated dispersion of the pigment which is subsequently diluted to form the final printing ink.

5 The dispersions typically contain from 5 to 95% by weight of the pigment, the precise quantity depending on the nature of the pigment and the quantity depending on the nature of the pigment and the relative densities of the pigment and the non-aqueous medium. For example, a dispersion which contains an organic pigment, preferably contains from 15 to 60% by weight of the solid whereas a dispersion in which the solid is
10 an inorganic pigment, preferably contains from 40 to 90% by weight of the pigment based on the total weight of dispersion.

The amount of The Dispersion is preferably from 10 to 100%, more preferably from 10% to 70% and especially from 20% to 50% based on the amount of pigment.

15 The dispersion may be obtained by any of the conventional methods known for preparing dispersions. Thus, the pigment, the non-aqueous medium and The Dispersant may be mixed in any order, the mixture then being subjected to a mechanical treatment to reduce the particles of the pigment to an appropriate size, for example by ball milling, bead milling, gravel milling or plastic milling until the dispersion is formed. Alternatively,
20 the solid may be treated to reduce its particle size independently or in admixture with either the non-aqueous medium or the dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If a composition containing pigment and The Dispersant is required in dry form, the non-aqueous medium is preferably volatile so that it may be readily removed from the particulate pigment by a simple separation means such as evaporation. It is preferred,
25 however, that the composition is a dispersion.

If the dry composition consists essentially of The Dispersant and a pigment, it preferably contains at least 0.2%, more preferably at least 0.5% and especially at least 1.0% dispersant based on weight of the pigment. Preferably the dry composition contains not greater than 100%, preferably not greater than 50%, more preferably not greater than
30 20% and especially not greater than 10% by weight based on the weight of the pigment.

The printing ink may additionally contain an RMV modifier which may be a Lewis acid, an organic or inorganic acid or a phenolic compound. Examples of RMV modifiers are acetic, citric, tartaric, toluic and p-naphthoic acids, naphthalene-2-sulphonic acid and p-toluene sulphonic acid; resorcinol and 2-naphthol; alkyl partial esters of phosphorus
35 acids and linear phenolic polymers such as novolak resins. The preferred RMV modifier is a novolak resin, especially those containing a 4-alkyl substituent and particularly those with a C₁₋₁₀- and especially a C₄₋₈-alkyl group. Useful effects have been obtained with Uravar FN5 as RMV modifier.

The most suitable RMV for any given printing ink can be readily determined using the protocol described in WO 97/15633 which protocol may also be used to establish the optimum amount of RMV modifier. The amount of RMV modifier in the ink is generally not greater than 10%, preferably not greater than 5% and especially not greater than 2%.

5 In view of the foregoing preferences an especially preferred printing ink according to the first aspect of the invention comprises a pigment, a dispersant of the Formula (1), a substantially non-aqueous medium and a RMV modifier as hereinbefore defined.

The printing inks according to the first aspect of the present invention preferably have a viscosity at 25°C of less than 50cP, more preferably less than 20cP, especially
10 less than 15cP and more especially from 7 to 15cP.

According to a second aspect of the present invention there is provided a process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to the first aspect of the invention.

The preferred inks used in this process are the preferred inks hereinbefore
15 described in relation to the first aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor
20 adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a piezoelectric crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably
25 paper, plastic, an overhead projector slide or a textile material.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper
30 (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper.

Preferred textile materials are natural, synthetic and semi-synthetic materials.
35 Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

A third aspect of the present invention provides a substrate printed with an ink according to the first aspect of the present invention, or by means of the process according to the second aspect of the present invention.

A fourth aspect of the present invention provides an ink jet printer cartridge containing an ink according to the first aspect of the present invention.

The invention is further illustrated by the following examples where all references to amounts are in parts by weight unless indicated to the contrary.

Examples 1 to 3 and Comparative Example A: Black Inks

Millbases were prepared having the composition outlined in Table 1 below by milling the components as indicated in the presence of glass beads (3mm, 125 parts) on a horizontal Red Devil shaker for 90 minutes. After milling, the beads were removed and the millbase diluted with oleyl alcohol (7.1 parts, Novol ex Croda Chemicals) and an aliphatic hydrocarbon mineral oil (28.4 parts, Lytol ex Witco) to give a printing ink.

The Receding Meniscus Velocity of the inks (RMV) was measured at 30°C using the method described in WO 97/15633. The results are given in Table 2 below which clearly show that the dispersants according to the present invention (Dispersants (1), (2) and (3)) provide inks which exhibit a superior (higher) RMV compared to Dispersant A (a comparative dispersant which has a weight ratio of $(T-(O-A-CO)_n)_p$ to Z is 3.5:1 and therefore outside the scope of the present invention).

Table 1

Example	1	2	3	A
Millbase	1	2	3	4
Regal 250R (pigment)	5.00	5.00	5.00	5.00
Dispersant 1	1.37	-	-	-
Dispersant 2	-	1.37	-	-
Dispersant 3	-	-	1.37	-
Dispersant A	-	-	-	1.71
Solsperse 5000 (fluidising agent)	0.09	0.09	0.09	0.09
Hydrocarbon solvent	3.54	3.54	3.54	3.20
	10.00	10.00	10.00	10.00

Footnote to Table 1

Regal 250R is carbon black pigment ex Cabot Corporation

Dispersant 1 is a 50% solution of PHS/PEI (7:1) in Lytol

Dispersant 2 is a 50% solution of PHS/PEI (10:1) in Lytol

Dispersant 3 is a 50% solution of PHS/PEI (13:1) in Lytol

Dispersant A is a 40% solution of PHS/PEI (3.5:1) in Lytol

5 Solperse 5000 is a quaternary ammonium salt of sulphonated copper phthalocyanine ex Zeneca Ltd.

Hydrocarbon solvent is Lytol ex Witco.

Dispersant A is made by the process described in Example 7/Agent H in GB 2 001 083.

10 Dispersants 1 to 3 are made by a similar process to that described for Dispersant A except that the ratio of poly(12-hydroxystearic acid) to polyethyleneimine (PHS/PEI) is as indicated in parenthesis.

Table 2

Millbase	Dispersant	RMV (mm/sec at 30°C)
1	1	8.9
2	2	10.0
3	3	8.7
4	A	7.9

15 Footnote to Table 2

Dispersants 1-3 and A are as hereinbefore described in the footnote to Table 1.

Examples 4 to 6 and Comparative Example B: Red Inks

20 Millbases were prepared containing a red pigment by a similar method to that described in Examples 1 to 3 by milling together the components listed in Table 3 below. These millbases were then diluted by adding aliphatic hydrocarbon solvent (27.0 parts, Lytol ex Witco). The RMV was again measured using the method described in WO 97/15633. The results are given in Table 4 and show that those inks prepared using dispersants with a higher PHS to PEI ratio exhibit superior RMV to inks prepared using
25 Dispersant A.

Table 3

Example	4	5	6	B
Millbase	5	6	7	8
Hostaperm Red E5B02	3.33	3.33	3.33	3.33
Dispersant 1	2.34	-	-	-
Dispersant 2	-	2.34	-	-
Dispersant 3	-	-	2.34	-
Dispersant A	-	-	-	2.92
Hydrocarbon solvent	4.33	4.33	4.33	3.75
	10.0	10.0	10.0	10.0

Footnote to Table 3

5 Hostaperm Red E5B02 is a red pigment ex Hoechst.

Dispersants 1 to 3, dispersant A and hydrocarbon solvent are as explained in the footnote to Table 1.

Table 4

Millbase	Dispersant	RMV (mm/sec at 30°C)
5	1	2.7
6	2	2.9
7	3	4.6
8	A	<1

10

Footnote to Table 4

Dispersants 1 to 3 and A are as hereinbefore described in the footnote to Table 1.

Example 7 and Comparative Example C: Blue Inks

15

A blue millbase was prepared by milling together the components listed in Table 5 below in a glass vial in the presence of 3mm glass beads (40 parts) for 4 hours on a Red Devil horizontal shaker.

	Example 4	Comparative Example C
Blue Pigment	3	3
Dispersant A	-	3
Dispersant 2	2.4	-
Solsperse 5000	0.3	0.3
Hydrocarbon Solvent	4.3	3.7

Footnote to Table 5

The Blue Pigment is Irgalite Blue GLVO ex Ciba-Geigy.

5 Dispersants A and 2 and Hydrocarbon Solvent are as explained in the footnote to Table 1.

10 The glass beads were then removed from the millbase which was let down by adding oleyl alcohol (13.3 parts, Novol ex Croda Chemicals) and hydrocarbon solvent (36.8 parts, Lytol ex Witco) to give a printing ink.

15 The RMV of each ink was determined using the method described in WO 97/15633. The ink prepared from the millbase of Example 4 exhibited an RMV of 5.9 compared with an RMV of 3.4 for the ink prepared from the millbase of Comparative Example C.

Example 8 and Comparative Example D: Blue Inks

20 A novolak resin (1 parts of 10% w/w solution of Uravar FN-5 in Lytol) was added to the printing ink prepared as described in Example 7 and Comparative Example C (10 parts) with RMV again measured. These are inks of Example 8 and Comparative Example D, respectively which exhibited RMV of 10.3 and 7.9, respectively. Again, the ink prepared using Dispersant 2 exhibited superior RMV to that prepared using Dispersant A.

Example 9 and Comparative Example E: Yellow Inks

25 Millbases were prepared in a similar manner to that described in Example 7 and Comparative Example C except using the components and amounts listed in Table 6 below.

Table 6

	Example 9	Comparative Example E
Yellow Pigment	3	3
Dispersant A	-	3
Dispersant 2	2.4	-
Hydrocarbon Solvent	4.6	4

Footnote to Table 6

5 The yellow pigment is Palitol Yellow D1155 ex BASF Dispersants 2 and A and Hydrocarbon Solvent are as explained in the footnote to Table 1.

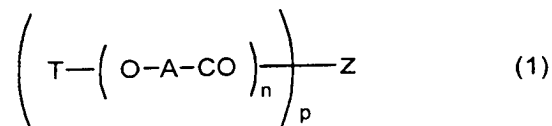
10 A printing ink was prepared by removing the beads and diluting with a letdown consisting of oleyl alcohol (10.8 parts) and hydrocarbon solvent (39.1 parts Lytol). The RMV of the ink prepared from the millbase of Example 9 was 10.2 and that prepared from the millbase of Comparative Example E was 9.3.

Example 10 and Comparative Example F: Yellow Inks

15 Novolak resin (1.25 parts of 10%w/w solution of Uravar FN-5 in Lytol) was added to the inks of Example 9 and Comparative Example E respectively to give inks of Example 10 and F. The RMV of the ink of Example 10 was 13.2 compared with 12.2 for the ink of Comparative Example F.

CLAIMS

1. A drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of formula 1



5

wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene;

Z is the residue of a polyamine or polyimine;

10

n is from 2 to 10;

p is not less than 2; and

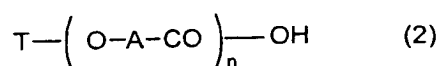
the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1; including salts thereof.

15

2. A printing ink as claimed in claim 1 wherein the weight ratio of (T-(O-A-CO)_n)_p to Z is from 9:1 to 13:1.

20

3. A printing ink as claimed in either claim 1 or claim 2 wherein the dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (TPOAC acid) of formula 2:



wherein T, A and n are as defined in claim 1.

25

4. A printing ink as claimed in claim 3 wherein the TPOAC acid is derived from 12-hydroxystearic acid.

30

5. A printing ink as claimed in either claim 3 or claim 4 wherein the number-average molecular weight of the TPOAC acid is from 800 to 2000.
6. A printing ink as claimed in any one of claims 1 to 5 wherein the number-average molecular weight of the polyamine or polyimine is from 5,000 to 100,000.

7. A dispersant as claimed in any one of the preceding claims wherein Z is the residue of polyethyleneimine.
8. A printing ink as claimed in any one of claims 1 to 7 wherein the non-aqueous medium is an aromatic or aliphatic hydrocarbon or mixtures thereof.
9. A printing ink as claimed in claim 8 which additionally comprises a C₁₀₋₃₀-aliphatic fatty alcohol.
10. A printing ink as claimed in any one of claims 1 to 9 wherein the non-aqueous medium has a solubility parameter of 7.0 MPa^{1/2} or less.
11. A printing ink as claimed in any one of claims 1 to 10 which additionally comprises a fluidising agent.
12. A printing ink as claimed in any one of claims 1 to 11 which additionally comprises a Receding Meniscus Velocity (RMV) modifier.
13. A printing ink as claimed in claim 12 where the RMV modifier is a linear phenolic polymer.
14. A printing ink according to any one of the preceding claims wherein the ink has a viscosity at 25°C of less than 50cP.
15. A process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to any one of the preceding claims.
16. A substrate printed with an ink according to any one of claims 1 to 14, or by means of the process according to claim 15.
17. An ink jet printer cartridge containing an ink according to any one of claims 1 to 14.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 00/00060

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 837 046 A (TATUM JOHN PHILIP ET AL) 17 November 1998 (1998-11-17) column 3, line 51-62; claims 1,2,4; example 1	1,3-11, 14-17
Y		12,13
Y	WO 97 15633 A (TATUM JOHN P ;WOODS JILL (GB); XAAR LTD (GB)) 1 May 1997 (1997-05-01) cited in the application page 8, line 1 -page 9, line 7	12,13
X	GB 2 001 083 A (ICI LTD) 24 January 1979 (1979-01-24) cited in the application page 2, line 51,52; example 23	1-8,10, 14,16
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

9 March 2000

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 00/00060

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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